

# Characterization of Graphite Anodes at Low Temperature by Pulse Power Testing and FTIR Spectroscopy

Hui Yang<sup>a</sup>, Guorong V. Zhuang<sup>b</sup>, and Philip N. Ross, Jr.<sup>b</sup>  
 Environmental Energy Technologies Division<sup>a</sup> and  
 Materials Sciences Division<sup>b</sup>,  
 Lawrence Berkeley National Laboratory, University of  
 California, Berkeley, CA 94720

The low temperature (LT) performance of lithium ion batteries is receiving increasing attention<sup>1-4</sup>. Graphite anodes have been identified as the limiting electrode in LT performance<sup>3,4</sup>. Along with other phenomena, Li deposition during charging at LT is believed to be responsible for permanent loss of capacity. We studied graphite anodes in two electrolytes: 1.2 M LiPF<sub>6</sub>/EC:EMC (3:7 wt%) (denoted as electrolyte A) and 1m LiPF<sub>6</sub>/EC:PC:DMC (1:1:3 wt%) (denoted as electrolyte B) by combining hybrid pulse power characterization (HPPC) and Fourier Transform Infrared (FTIR) spectroscopy.

Graphite anodes (MAG-10) were assembled into Li/graphite half-cells in electrolytes A and B and subject to two galvanostatic charge/discharge formation cycles between 1.0 V and 0.01 V vs. Li/Li<sup>+</sup> at C/25. Prior to HPPC tests, anodes thus formed at room temperature (RT) were fully intercalated and then deintercalated to 50% of depth of discharge (DOD) at C/25. We modified ambient HPPC test protocol<sup>5</sup> by decreasing the pulse current and duration to avoid cell degradation and access Li deposition during charging (intercalation) at LT. First a 10 s discharging pulse at current density of 1.5 mA·cm<sup>-2</sup> (1 C rate) was applied to the cells. After 32 s resting period, a 2s charging pulse at current density of 0.3 mA·cm<sup>-2</sup> (C/5) was applied. Immediately upon completion of the charging pulse, the DOD of the cells was then increased by 5% at current density of 0.15 mA·cm<sup>-2</sup> (C/10). This sequence, separated by one-hour resting period to allow cells return to an equilibrium condition, was repeated until final potential reaches 1V vs. Li/Li<sup>+</sup>. The rates used in HPPC tests were based on 2<sup>nd</sup> de-intercalation capacity in the formation cycle at RT.

The HPPC test results at 30 °C and -30 °C are presented in Fig. 1 panel A and panel B, respectively. Although both cells showed very similar voltage profiles at 30 °C, cell A exhibited much higher resistance and polarization than cell B at -30 °C. During 2s C/5 charging pulse, the voltage of cell A dropped far below -0.2 V (vs. Li/Li<sup>+</sup>), while that of cell B only reaching -0.02 V (vs. Li/Li<sup>+</sup>). Polarization during charging pulse in electrolyte A is three times large than that in electrolyte B at -30°C. To gain insights on the consequence of large polarization at LT, we further characterized graphite anodes subject to HPPC tests by FTIR spectroscopy.

The FTIR spectra on graphite anodes in electrolyte A after HPPC at 30 °C and -30 °C are shown in Fig. 2. While there is no spectroscopic evidence of Li deposition on graphite anode in electrolyte B, a strong peak at 1640 cm<sup>-1</sup> (marked by the arrow) characteristic of SEI on metallic Li appears on graphite anode after HPPC tests in electrolyte A at -30°C. We also established by FTIR spectroscopy that larger polarization and consequent Li deposition in electrolyte A are not due to differences in SEI layer formed in those two electrolytes, i.e. the SEI layers have identical compositions and thicknesses. Results from electrochemical and spectroscopic study will be presented and discussed in detail.

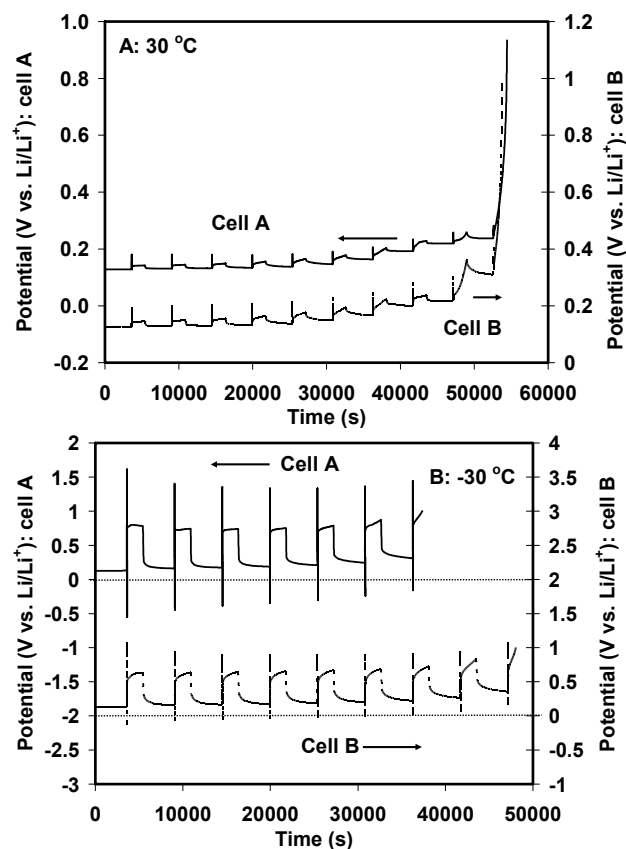


Figure 1. The HPPC profiles of graphite anodes at various state of DOD starting from 50% in electrolytes A and B at 30 °C and -30 °C.

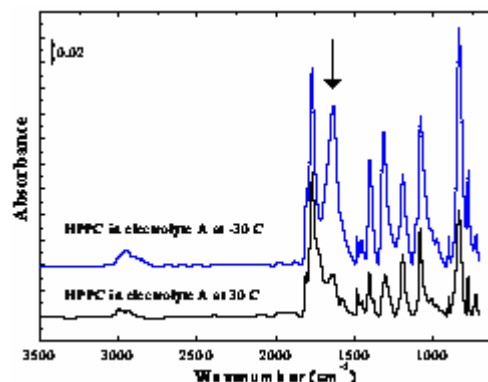


Figure 2. FTIR spectra of graphite anodes in electrolyte A after HPPC test at 30 °C and -30 °C.

**Acknowledgements** This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We thank Drs. S. S. Zhang, K. Xu and T. Richard Jow of Army Research Lab for supplying the LT electrolyte used in this work.

## References

1. T. R. Jow, M. S. Ding, K. Xu, S. S. Zhang, J. L. Allen, K. Amine, G. L. Henriksen, *J. Power Sources*, 119-121, 343 (2003).
2. M. C. Smart, B. V. Ratnakumar, L. D. Whitcanack, K. B. Chin, S. Surampudi, H. Croft, D. Tice and R. Staniewicz, *J. Power Sources*, 119-121, 349 (2003).
3. C.-K. Huang, J. S. Sakamoto, J. Wolfenstine and S. Surampudi, *J. Electrochem. Soc.*, 147, 2893 (2000).
4. H.-P. Lin, D. Chua, M. Salomon, H.-C. Shiao, M. Hendrickson, E. Plichta and S. Slane, *Electrochem. Solid-State Lett.*, 4, A71 (2001).
5. FreedomCAR Battery Test Manual for Power-Assist Hybrid Electric Vehicles, DOE/ID-11069, October 2003.